

Gaseous Combustion at High Pressures. Part II.—The Explosion of Hydrogen-Air and Carbon Monoxide-Air Mixtures.

By WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S., and the late WILLIAM ARTHUR HAWARD, M.Sc., Salters' Research Fellow.*

(Received June 14, 1921.)

Introduction.

In a previous paper upon the subject,† the question was propounded whether or no there is any direct relation between the actual rate at which the potential energy of an explosive mixture is transferred on explosion as sensible heat to its products and the magnitude of the chemical affinity between its combining constituents. As the result of an experimental enquiry into the matter, it was proved:—

(a) that, whereas the affinity for oxygen of methane is at least twenty to thirty times greater than that of hydrogen, the time required for the attainment of maximum pressure in the case of the primary methane-air mixture ($\text{CH}_4 + \text{O}_2 + 4\text{N}_2$) is at least some five to eight times as long as that required in the case of the primary hydrogen-air mixture ($2\text{H}_2 + \text{O}_2 + 4\text{N}_2$);

(b) that whereas in mixtures corresponding to $\text{CH}_4 + \text{O}_2 + x\text{H}_2$ (in which x was varied between 2 and 8), the "mass influence" of successive increases in x upon the actual oxygen distribution between the two combustible gases is proportional to x^2 , yet in mixtures corresponding to $\text{CH}_4 + \text{O}_2 + x\text{CO}$ it is nearly proportional to x ; or, in other words, whilst the "mass influence" of hydrogen is proportional to the square, that of carbon monoxide is in accordance with the first power, of its concentration;

(c) that in hydrogen-air and carbon monoxide-air mixtures corresponding to $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ and $2\text{CO} + \text{O}_2 + 4\text{N}_2$, respectively, in which the com-

* This paper had been drafted for communication to the Royal Society only a few days before the occurrence of the accident in my laboratory (December 6, 1920) which so tragically ended poor Haward's life. He was suddenly struck down by death whilst actually engaged upon some final experiments designed to test and develop some of the theoretical issues set forth in the concluding paragraphs. This further part of the work will have to be completed by other hands than his, now that the apparatus has been overhauled and its damaged parts made good. Meanwhile, Haward's experimental results are being published in practically the same form as he last reviewed them with me, not only because of their exceptional interest, but also as a tribute to his great experimental skill and passionate devotion to scientific research. He laid down his life in the cause of science at the age of 26 years. A short sketch of his distinguished career appeared in 'Nature,' on December 16, 1920.—W. A. B.

† W. A. Bone and others, 'Phil. Trans.,' A, vol. 215, p. 275.

bustible gas and oxygen are present in their combining proportions, and which on explosion develop practically the same total energy (equivalent to 68.4 K.C.U. per gram-molecule in the case of hydrogen, and 68.0 in the case of carbon monoxide), the time taken for the attainment of the maximum pressure on explosion is at least ten times longer in the case of carbon monoxide than in that of hydrogen.

It thus appeared that the rate at which the potential energy of an explosive mixture is transferred into thermal energy, as measured by the rise in pressure when the explosion is carried out in a closed vessel, is not primarily determined by the chemical affinity between the combustible gas and oxygen, as ordinarily understood, but by some other factor or circumstance, then unknown, and which, therefore, required closer investigation. The present paper embodies the results of further experiments upon the matter.

Experimental.

Apparatus and Experimental Method.—The apparatus and methods employed in these further experiments have been substantially the same as those already described in the previous paper.* Seeing, however, that it was now desired always to obtain optical records of the complete pressure curves on exploding the various experimental mixtures, we employed throughout the spherical bomb B,† to which was attached the Petavel recording manometer with its optical accessories.‡ The bomb had a spherical cavity 3 inches in diameter (capacity approximately 275 c.c.), which, when fitted with its coned admission valve, ignition plug, and the Petavel manometer, was easily capable of holding up a pressure of 600 atmospheres. The reader is referred to the former paper for details concerning (a) the mode of admitting and mixing the various constituents of the gaseous mixture at the outset of each experiment, (b) the ignition device, and (c) the optical recording of the pressure during the explosion which followed. An electrically controlled tuning-fork, giving 100 vibrations per second, was employed as a time indicator, the fork being so placed that each vibration momentarily interrupted the light falling on to the photographic film of the pressure-recording apparatus, thus producing a dotted instead of a continuous pressure curve. We were thus able to measure the time taken in each experiment for the attainment of maximum pressure to within 0.005 second, but not much closer, which however, was sufficiently

* *Loc. cit.*, pp. 276–287 and 314–15.

† *Loc. cit.*, figs. 5 and 6.

‡ *Loc. cit.*, figs. 14 and 15.

accurate for our purpose.* Certain minor improvements made in the optical arrangements since the previous research enabled us to obtain even better pressure records, which could therefore be read and measured with somewhat greater accuracy than before. The ratio of the *maximum* to the *initial* pressure could usually be determined to within about 1 per cent. of the true value, or, say, to the first decimal place.

The substantial purity of the gases employed for making the various experimental mixtures was in each case always established by chemical analysis. The nitrogen and hydrogen used had been bought from trustworthy sources in cylinders under 100 atmospheres pressure. The carbon monoxide and oxygen were prepared in the laboratory (by methods already described in the previous paper),† and then compressed on the spot into cylinders up to 100 atmospheres before use.

Altogether fifty-two experimental mixtures, the exact composition of which was subsequently determined by analysis, were exploded in the bomb, each at an initial pressure of 50 atmospheres. The results of the first twenty were, however, discarded as being somewhat less reliable than the rest; because of a suspicion that in some of them there might have been a slight lag in the rising pressure curve due to a possible sticking of the moving parts of the Petavel manometer, which was thereupon thoroughly cleaned and overhauled. With one or two exceptions, the records obtained in the remaining thirty-two experiments, when the manometer was working at its maximum sensitiveness, were all remarkably clear and concordant; the results of some eighteen of them were finally selected for the purpose of this paper.

During the course of the research, the tightness of the bomb, and the condition of the surface of its explosion chamber, were frequently tested by exploding in it mixtures of oxygen with excess of hydrogen. This precaution was always necessary after any experiment in which (as was sometimes the case) an experimental mixture containing an excess of oxygen had been exploded, with consequent possible slight oxidation of the walls of the explosion chamber. Such experiments were, therefore, always followed by a

* In amplification of this statement, it may be explained that the recording apparatus enabled us to measure quite definitely 0.005 sec., which in most of the experiments was less (and in some considerably so) than the time actually taken to attain the maximum pressure. And in such cases the record of the pressure curve obtained was invariably a line free from any sign of "vibration" either in passing through or after attaining the maximum point. On the other hand, in one or two experiments, in which the maximum pressure was attained in less than 0.005 sec., the record showed some sign of such vibration just after the maximum had been reached.

† *Loc. cit.*, p. 277.

series of oxygen with excess hydrogen explosions, until the resulting contraction was observed to be exactly equal to three times the partial pressure of the oxygen originally taken.

More than forty optical calibrations were made of the Petavel manometer during the research, from which the various optical explosion pressure records were subsequently gauged.

It was assumed that any slight deviation of the four diatomic gases, hydrogen, carbon monoxide, nitrogen, and oxygen, from Boyle's law, within the experimental condition, might be considered as negligible for all practical purposes; and actual trials in the bomb of the compressibilities of hydrogen and nitrogen, respectively, confirmed this view. In cases where mixtures containing carbon monoxide were exploded, the observed final pressure of the cold products (P_f) were always "corrected" for the ascertained deviation of their carbon dioxide-content from the law.

In the tabulated experimental results:—

P_i = the initial pressure in atmospheres at which each mixture was fired.

P_m = the maximum pressure in atmospheres attained in the explosion.

P_f = the final pressure in atmospheres of the cooled products of combustion.

P_k = the actual pressure in atmospheres of the real "knall-gas."

t_m = time in seconds taken for the attainment of maximum pressure after ignition.

Σ = the thermal equivalent in K.C.U. of the total energy liberated during the explosion.

1ST SERIES.—*Experiments with Mixtures* $2H_2 + O_2 + 4X_2$ (where $X_2 = N_2, H_2, \text{ or } O_2$).

In each of these experiments, the object of which was to find to what extent (if at all) the rate of attainment of maximum pressure in an hydrogen air mixture ($2H_2 + O_2 + 4N_2$) would be affected by the substitution for the diluent nitrogen of an equivalent molecular proportion of hydrogen or oxygen, the original mixture was fired at an initial pressure of 50 atmospheres. It was very difficult, indeed hardly possible, always to make the mixtures of *exactly* the intended composition; but by selecting for comparison those in which the difference between the initial and final pressures of the cold mixture and products, respectively, was as nearly as possible equal to 21.4 atmospheres, any experimental error due to such cause was minimised.

The results of six typical experiments are tabulated on p. 71.

Table I.—Results of Experiments (1st Series) with $2\text{H}_2 + \text{O}_2 + 4\text{X}_2$ Mixtures.

Experiment	I.	II.	III.	IV.	V.	VI.
Mixture	$2\text{H}_2 + \text{O}_2 + 4\text{N}_2$.			$2\text{H}_2 + \text{O}_2 + 4\text{O}_2$.	$2\text{H}_2 + \text{O}_2 + 4\text{H}_2$.	
Initial temp., C. ...	18·5°	17·5°	14·7°	22·5°	11·0°	11·0°
Pressures in atmos. $\left\{ \begin{array}{l} P_i \dots\dots \\ P_k \dots\dots \\ P_f \dots\dots \\ P_m \dots\dots \end{array} \right.$	50·0	50·0	50·0	50·0	50·0	50·0
	21·7	21·2	21·7	21·5	21·8	21·7
	28·8	28·5	28·3	28·8	28·2	27·5
	405	391	402	400	408	408
Ratio P_m/P_i	8·1	7·8	8·04	8·0	8·16	8·16
t_m secs.	0·005			about 0·010	about 0·0025	
Σ K.C.U.	10·45	10·18	10·50	10·33	10·48	10·40

We succeeded in obtaining three exceptionally good records of the pressure-curves in the hydrogen-air ($2\text{H}_2 + \text{O}_2 + 4\text{N}_2$) mixtures, one of which (Experiment I) is reproduced in fig. 1. They each showed an almost instantaneous rise (in about 0·005 second) to the maximum pressure of about 400 atmospheres, the attainment of which was immediately succeeded by the commencement of the cooling period. The cooling curves, however, all gave some indication of there having been a slight evolution of heat during a short period (about 0·10 second) after the actual attainment of the maximum pressure, thereafter becoming straight lines.*

It is of interest to compare our time-pressure curve with the time-temperature curve deduced by Prof. W. T. David from his recent experiments on "Radiation in Explosions of Hydrogen and Air"† for the explosion of a mixture of nearly the same composition (a 25·4 per cent. hydrogen mixture) as ours in a closed vessel with blackened walls at atmospheric pressure. His maximum temperature (2400° C. abs.) was reached in 0·017 sec. after ignition; and his cooling curves gave no indication of any heat evolution occurring in the system after the maximum temperature had been passed. He also found that the mixture in question lost as much as 16·1 per cent. of its total potential energy (heat of combustion) by radiation, nearly the whole of which was emitted during the cooling period at a rate approximately

* In the previous paper (*loc. cit.*, pp. 316 and 317) the time observed for the attainment of maximum pressure for similar mixtures of $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$, when fired in the bomb at initial pressures of 50 atmospheres, was 0·010 sec., and the succeeding cooling-curve (*q.v.*) was practically a straight line throughout. This slight difference between the new and the old results is to be ascribed to the somewhat greater sensitiveness of the pressure-recording part of the apparatus in the present research than formerly.

† 'Proceedings,' A, vol. 98, p. 185 (1920).

proportional to the fourth power of the absolute temperature. It may

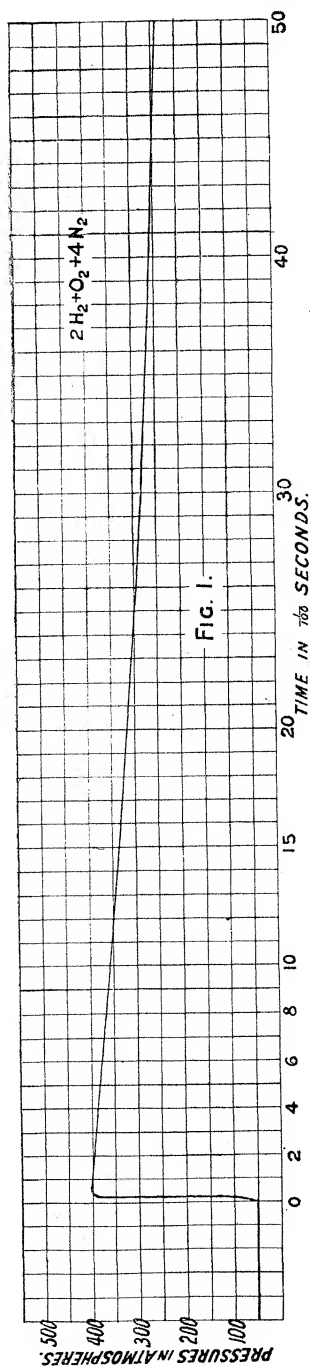


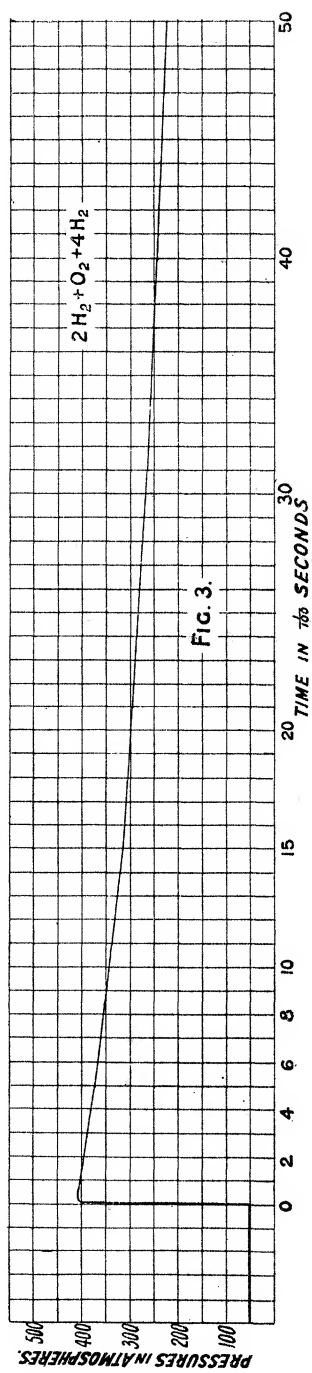
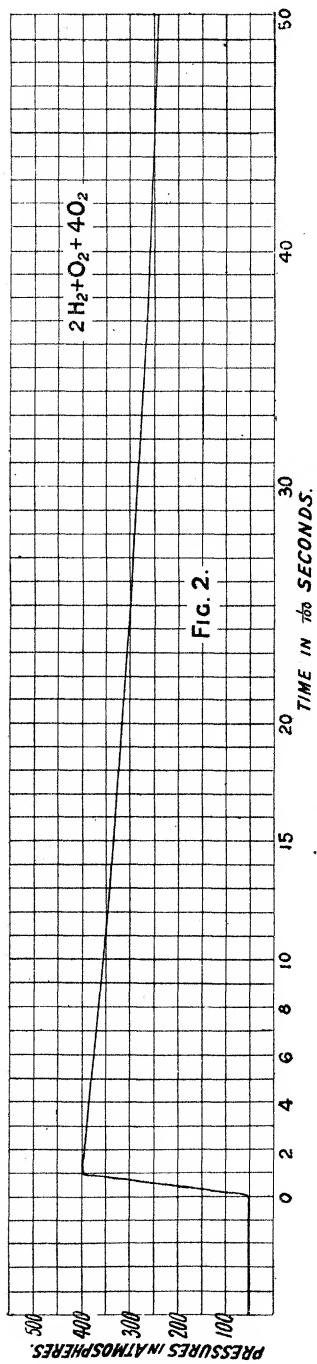
Fig. 1.

also be noted that, whereas until the temperature had fallen to $1,200^{\circ}$ C. abs. this radiation consisted chiefly of the 2.8μ band of "steam" (as found in a hydrogen flame), at the highest temperature ($2,400^{\circ}$ to $2,200^{\circ}$ C. abs.) some radiation of shorter wave was emitted; also that below $1,200^{\circ}$ C. abs. (at which the 2.8μ line had almost ceased) some of greater wave-length could be detected. The fact that the emission of radiation of shorter wave-lengths than 2.8μ has been detected at the highest temperature during hydrogen-air explosions seems to us to be of some significance in connection with the theory of combustion, suggesting, as it does, the initial transitory formation of an intensely vibratory complex when hydrogen and oxygen combine in flames, a consideration that will be referred to again in the concluding part of the paper.*

From Table I, it will be seen that the substitution of hydrogen or oxygen for nitrogen as the diluent gas had no very marked influence upon the course of the explosion; if anything, the substitution of hydrogen quickened, and that of oxygen somewhat retarded, the attainment of the maximum pressure. Also, the substitution of hydrogen tended to quicken slightly the cooling, as, indeed, might be expected from its greater heat conductivity and mobility than nitrogen. Two typical curves, one for

* Professor David himself rather suggested that it might be due to the presence of nitrogen in the exploded gases, because nitrogen gives a strong emission band at 1μ in a vacuum tube (*loc. cit.*, p. 192, footnote); but it may be doubted whether nitrogen would become emissive in an explosion,

and the above interpretation seems to be the better one.



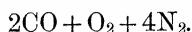
the mixture $2\text{H}_2 + \text{O}_2 + 4\text{O}_2$ (Experiment IV), and the other for the mixture $2\text{H}_2 + \text{O}_2 + 4\text{H}_2$ (Experiment V), are reproduced in figs. 2 and 3 respectively; and in Table II the three curves are analysed.

Table II.—Analysis of Curves shown in Figs. 1, 2 and 3.

t , (secs. after ignition).	Fig. 1. Experiment I.	Fig. 2. Experiment IV.	Fig. 3. Experiment V.
	$2\text{H}_2 + \text{O}_2 + 4\text{N}_2$.	$2\text{H}_2 + \text{O}_2 + 4\text{O}_2$.	$2\text{H}_2 + \text{O}_2 + 4\text{H}_2$.
	P. atmos.	P. atmos.	P. atmos.
0·000	50	50	50
0·025 to 0·010*	405	400	408
0·050	385	380	371
0·100	358	355	343
0·150	337	337	320
0·200	317	320	300
0·300	282	288	267
0·400	260	263	242
0·500	237	242	222
0·600	218	221	204
0·700	198	205	189
0·800	185	190	—
0·900	174	179	—
1·000	164	168	—

* This represents t_m , the time taken for the attainment of P_m , which varied between 0·0025 and 0·010 sec. in the different experiments (*vide* Table I).

2ND SERIES.—*Experiments with Carbon Monoxide-Air Mixtures*



For comparison with the behaviour of the foregoing hydrogen-air mixtures (Experiments I to III inclusive), the following three experiments (VII to IX inclusive) with CO-air mixtures ($2\text{CO} + \text{O}_2 + 4\text{N}_2$), liberating the same total amount of energy on combustion, were made. Unfortunately, the original mixture in Experiment VII was afterwards found to have been weaker ($\text{CO} = 26\cdot35$ instead of $28\cdot6$ per cent.), and that in Experiment IX slightly stronger ($\text{CO} = 30\cdot1$ instead of $28\cdot6$ per cent.) than had been intended. In Experiment VIII, however, the mixture was of exactly the right composition, and therefore its results were finally selected for detailed comparison with those of the correspondingly best experiment with the hydrogen-air mixture (Experiment I, *q.v.*). In all cases most excellent records were obtained of the pressure curves, one of which (from Experiment VIII) is reproduced in fig. 4 and analysed in detail. The results of the whole series are epitomised in Table III.

Comparing now figs. 1 and 4, it will at once be seen how strikingly dissimilar was the whole course of the combustion and subsequent cooling, although the total energy developed was as nearly as possible the same, in the two cases. In the case of the CO-air mixture (fig. 4), not only was the ratio P_m/P_i distinctly higher, but the time taken for the attainment of maximum pressure (t_m) was about thirty-six times longer than in the corresponding experiment (fig. 1) with the H_2 -air mixture. It may here be stated that there were indications that the time in question was not quite so constant in the CO-air series as it had been in the H_2 -air series, being apparently influenced to some extent by the hygroscopic state of the mixture, as, indeed, might be expected from H. B. Dixon's well-known work on the combustion of carbon monoxide. It is intended, in future experiments, to investigate this particular point more fully, as it appears to be of practical interest in connection with internal combustion engine problems.

Another notable difference between the two curves in question is that, whereas in the case of the hydrogen-air mixture, the cooling commenced almost immediately after the attainment of the maximum pressure, in the case of the CO-air mixture it was delayed for quite an appreciable time interval thereafter, showing that heat energy was still being liberated long after the maximum temperature had been reached. Also, the subsequent rate of cooling after t_m was very much slower in the CO-air than in the H_2 -air series. Indeed, nothing could be more strikingly different than the modes of combustion of carbon monoxide and

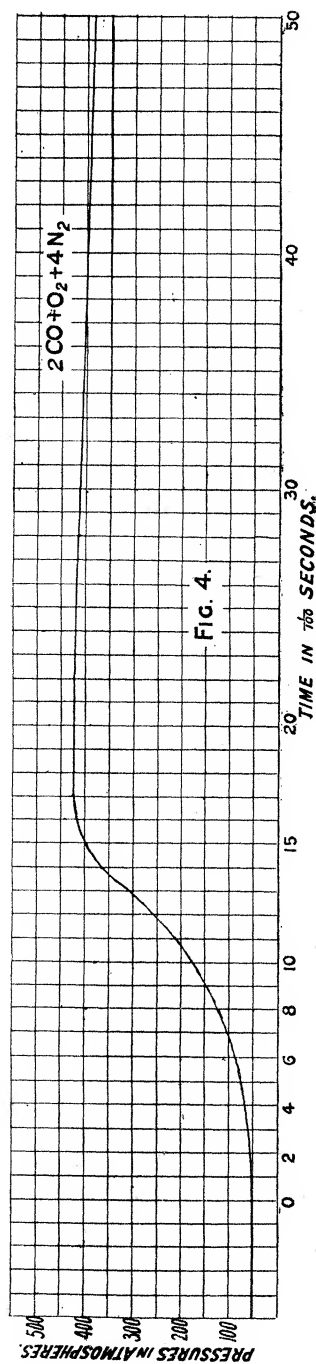


Table III.—Results of Experiments (2nd Series) with $2\text{CO} + \text{O}_2 + 4\text{N}_2$ Mixtures.

Experiment	VII.	VIII.	IX.
Per cent. CO in the mixture	26·35	28·6	30·1
Initial temp., C.	16·5°	18·2°	18·5°
Pressures in atmos. $\left\{ \begin{array}{l} P_i \\ P_k \\ P_r \text{ (corrected)} \\ P_m \end{array} \right.$	$\begin{array}{l} 50\cdot00 \\ 19\cdot75 \\ 41\cdot80 \\ 378 \end{array}$	$\begin{array}{l} 50\cdot00 \\ 21\cdot45 \\ 41\cdot50 \\ 421 \end{array}$	$\begin{array}{l} 50\cdot00 \\ 22\cdot50 \\ 41\cdot66 \\ 410 \end{array}$
Ratio P_m/P_i	7·56	8·42	8·2
t_m secs.	0·24	0·18	0·19
Σ K.C.U.	9·43	10·23	10·78

hydrogen as revealed by these two curves. An analysis of the CO-air curve (fig. 4) is given below:—

Analysis of CO-Air Pressure Curve. (Fig. 4.)

Time (secs.) after ignition	0·00	0·05	0·10	0·15	0·18	0·20	0·25	
Pressure (atmos.)	50	76	173	398	421	421	416	
Time (secs.) after ignition	0·30	0·40	0·50	0·60	0·70	0·80	0·90	1·00
Pressure (atmos.)	412	395	383	373	362	352	342	332

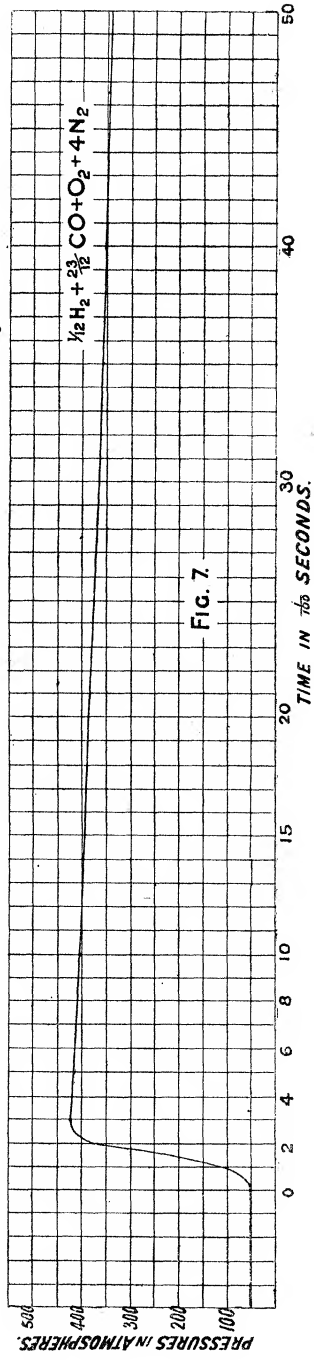
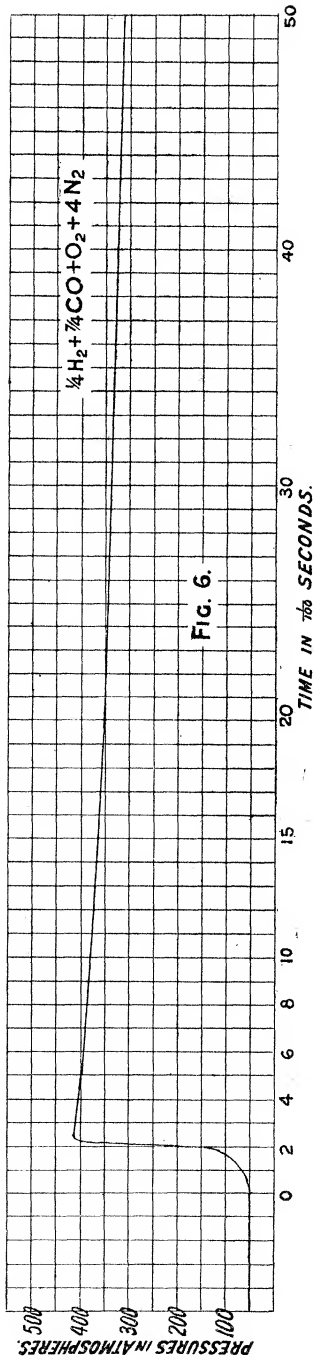
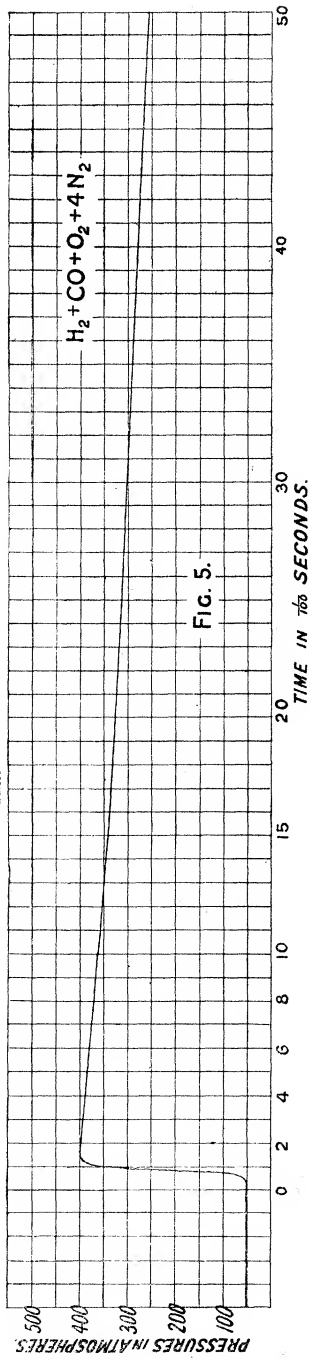
Indeed, a detailed comparison between the results of the two sets of Experiments I to IV (with H_2 -air mixtures) and VII to IX (with CO-air mixtures) respectively, has shown that, in the latter, not only was there always an interval of about 0·05 second, during which the maximum pressure was fully maintained, but also, subsequently, the pressure fell at only half the rate it had done in the former.

3RD SERIES.—Experiments with Isothermic Mixtures $2(m\text{H}_2 + n\text{CO}) + \text{O}_2 + 4\text{N}_2$.

It now seemed important to determine whether or not the marked disparity observed in the preceding series of experiments between the rates of attainment of maximum pressure in the H_2 -air and CO-air mixtures, respectively, can be ascribed to some difference in the molecular properties of the two combustible gases concerned. If so, then their separate influences upon the rate of attainment of maximum pressure should be *additive* when isothermic mixtures $2(m\text{H}_2 + n\text{CO}) + \text{O}_2 + 4\text{N}_2$ (where m and n are variable,

TABLE IV.
Results of Experiments (3rd Series) with Isothermic Mixtures 2 ($m\text{H}_2 + n\text{CO}$) + $\text{O}_2 + 4\text{N}_2$.

Expt.	Approximate mixture.	Percentage composition of the mixture				Initial temperature, C.	Pressures in atmos.		Ratio P_m/P_i	t_m (secs.) observed.	t_m (secs.) calculated on supposition of additive effects.	Σ K.C.U.
		CO.	H ₂ .	O ₂ .	N ₂ .		P _i .	P _m .				
II	$2\text{H}_2 + \text{O}_2 + 4\text{N}_2$	Nil	28.20	14.50	57.30	17.5	50	391	7.82	0.005	—	10.18
X	$\left\{ \begin{array}{l} \text{H}_2 + \text{CO} + \text{O}_2 + 4\text{N}_2 \dots\dots \end{array} \right\}$	14.5	13.0	15.1	57.4	20.5	50	399	7.98	0.015	0.092	9.87
XI		13.65	13.85	14.90	57.60	20.4	50	390	7.80			
XII	$\frac{1}{3}\text{H}_2 + \frac{2}{3}\text{CO} + \text{O}_2 + 4\text{N}_2$	19.90	6.70	14.55	58.85	21.5	50	410	8.2	0.015	0.136	9.54
XIII	$\left\{ \begin{array}{l} \frac{1}{4}\text{H}_2 + \frac{3}{4}\text{CO} + \text{O}_2 + 4\text{N}_2 \dots \end{array} \right\}$	21.95	3.55	14.20	60.30	20	50	409	8.2	0.025	0.158	9.12
XIV		22.90	3.60	14.30	59.20	20	50	418	8.86			
XV	$\left\{ \begin{array}{l} \frac{1}{8}\text{H}_2 + \frac{13}{8}\text{CO} + \text{O}_2 + 4\text{N}_2 \end{array} \right\}$	24.60	2.20	14.00	59.20	13	50	427	8.54	0.025 to 0.030	0.165	9.60
XVI		24.80	2.00	13.80	59.40	14	50	425	8.50			
XVII	$\left\{ \begin{array}{l} \frac{1}{12}\text{H}_2 + \frac{23}{12}\text{CO} + \text{O}_2 + 4\text{N}_2 \end{array} \right\}$	25.60	1.45	14.05	58.90	14.5	50	417	8.34	0.030	0.173	9.69
XVIII		25.50	1.10	14.30	59.10	13	50	425	8.50			
VIII	$2\text{CO} + \text{O}_2 + 4\text{N}_2$	28.6	Nil	16.0	55.4	18.2	50	421	8.40	0.180	—	10.23



but $m+n=1$) are exploded at the same initial pressure. On the other hand, if their effects are not additive, then the cause of the disparity in question must be sought for elsewhere.

All that was needed to settle experimentally this fundamental issue was to explode a series of such isothermic mixtures at the same initial pressure (50 atmospheres), and, from the pressure records, to compare the time actually taken in each case for the attainment of maximum pressure with that calculated on the supposition that the separate influences of hydrogen and of carbon monoxide are additive. This was accordingly done in the series of experiments in Table IV, with results which were certainly conclusive against any such supposition.

The very decisive character of these results will be made clear by a comparison of the pressure curves (figs. 5, 6, and 7) obtained in Experiments X, XIV, and XVIII, respectively, with those already reproduced (figs. 1 and 4, respectively) in connection with the H_2 -air and CO-air series, respectively.

It will be observed that in each of the above curves the sharp and almost vertical rise up to the point of maximum pressure, and the abrupt turning downwards thereafter, closely resemble the hydrogen-air curve (fig. 1, *q.v.*). Indeed, there was hardly any feature in the rising-pressure curves to suggest the influence of carbon-monoxide, except perhaps in the case of mixtures

Table V.—Analyses of the Pressure Curves in 3rd Series.

Experiment	II.	X.	XII.	XIV.	XVI.	XVIII.	VIII.
Ratio H_2 :CO in the mixture exploded	2:0	1:1	1:3	1:7	1:11	1:23	0:2
t , (secs. after ignition).	P. atmos.	P. atmos.	P. atmos.	P. atmos.	P. atmos.	P. atmos.	P. atmos.
0·000	50	50	50	50	50	50	50
0·005	391*	—	175	—	—	—	—
0·010	—	350	350	65	63	—	—
0·015	385	399*	410*	—	—	—	—
0·020	—	—	—	—	108	—	—
0·025	380	395	405	418*	—	—	55
0·030	—	—	—	—	425*	425*	—
0·050	368	382	397	399	415	418	75
0·100	340	362	380	381	398	403	175
0·200	298	327	354	357	379	382	421*
0·300	264	302	333	341	363	365	412
0·400	242	278	318	327	349	352	395
0·600	198	243	291	307	327	332	373
0·800	174	219	270	289	309	312	352
1·000	152	194	248	273	292	298	332

* The asterisk denotes the attainment of the maximum pressure (P_m) in each case.

containing more than seven volumes of CO to one of H₂, where it could just be traced for something like 0.005 second after ignition, during which the initial part of the rising curve was a little rounded. All this means that, in some way or other which has yet to be explained, the presence of even 1 per cent. (and probably less) of hydrogen in a CO-air mixture, at the high initial pressures employed by us, has an altogether disproportionately large influence in accelerating the rise of pressure on explosion. Indeed, such a small proportion of hydrogen seems capable of imposing its own character upon the whole course of the subsequent combustion at such pressures.

Analyses of the cooling curves obtained in this series (*vide* Table V) are of some interest, in that they show very distinctly how the progressive replacement of steam by carbon dioxide in the products retarded the pressure-fall after the maximum point had been passed.

Discussion of Results.

(1) To chemists who have specially studied gaseous combustion, there has always been something peculiarly enigmatical about the very different behaviour, in many respects, of the two simplest combustible gases, carbon monoxide and hydrogen. And even those who have not gone very deeply into the matter must have been struck with certain obvious differences between their flames.

This enigma may perhaps best be expressed by saying that, whilst the volumetric heats of combustion of the two gases, and also the volumetric proportion in which each of them combines with oxygen, are the same:—

$$\begin{array}{l} \text{e.g., we usually} \left\{ \begin{array}{l} 2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} \dots 68.4 \\ 2\text{CO} + \text{O}_2 = 2\text{CO}_2 \dots 68.0 \end{array} \right\} \begin{array}{l} \text{K.C.U. per gramme} \\ \text{molecule,} \end{array} \\ \text{write} \end{array}$$

yet in almost all other respects their modes of combustion present a strikingly wide contrast.

(2) Thus, for example, (*a*) hydrogen-air mixtures have lower ignition temperatures, and, under similar physical conditions, propagate flame much faster than the corresponding CO-air mixtures; (*b*) the flame of hydrogen burning in air is smaller and “sharper” than a similar flame of carbon monoxide (*i.e.*, burning at the same orifice and under the same pressure); indeed, the CO-flame is always described as being “lambent,” and its appearance suggests a *slower burning* gas than hydrogen; and (*c*) when corresponding H₂-air and CO-air mixtures are respectively exploded in a closed vessel, the pressure rises to a maximum *rapidly* in the case of hydrogen, but *slowly* in the case of carbon monoxide.

(3) These three contrasts all suggest that carbon monoxide has greater difficulty than hydrogen in getting oxidised in flames. In fact, ever since

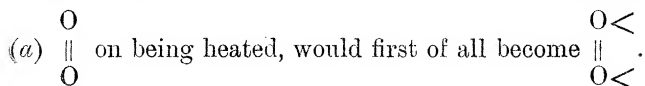
H. B. Dixon's classical researches, it has been known that the presence of even a minute quantity of steam greatly assists, if it is not absolutely essential to, the oxidation of carbon monoxide in flames. And it can easily be shown that a flame of the *dry* gas is extinguished on being introduced into a jar of air that has been dried over strong sulphuric acid. The precise mode in which steam accelerates or determines the combustion of carbon monoxide has, up to the present, never been completely explained; but chemists are generally agreed that the phenomenon in question is due to some peculiar inertness of CO for O₂ molecules in flames, which the presence of steam, somehow or other, overcomes. We are, therefore, justified in concluding that, in ordinary flames, carbon monoxide cannot interact with undissociated O₂ molecules.

(4) Another very significant difference between the respective behaviours of hydrogen and carbon monoxide in flames, which has already been referred to in the introductory portion of our paper, is the fact (first published by one of us in 1916) that, whilst what may be termed the "mass influence" of hydrogen upon the actual distribution of oxygen between the combustible constituents of a burning mixture is proportional to the *square* of its concentration, that of carbon monoxide is nearly proportional to the *first power* of its concentration. This can hardly mean otherwise than that, whereas the primary oxidation of hydrogen in flames involves the simultaneous action of two H₂ molecules, the primary oxidation of carbon monoxide does not require the action of more than one CO molecule.

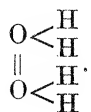
(5) Finally, in view of what has been brought to light during our present investigation, there must now be added to the other puzzling features of the problem the peculiar influence of hydrogen in accelerating the rise of pressure in the explosion of (H₂+CO)-air mixtures at high pressures, an effect which has been shown to be altogether disproportionate to the volumetric amount of it present.

(6) Although a complete explanation of the foregoing facts is hardly yet possible, in the present state of our knowledge, we venture to put forward the following view tentatively, as worthy of consideration, in the hope that it may provoke and stimulate further discussion and research. It involves the conception that, whereas in certain cases of combustion (such as that of hydrogen), undissociated O₂ molecules can, and ordinarily do, interact directly with those of the combustible gas, yet in other cases (such as that of carbon monoxide), the dissociation of the O₂ molecules is a necessary precedent to the actual oxidation; or, in other words, that oxygen in flames may function in two distinct ways, namely (*a*), as undissociated O₂, and (*b*) as dissociated and atomic O.

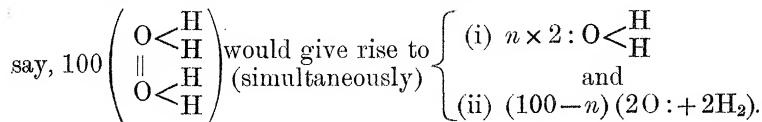
(7) According, then, to this conception, it may be supposed that an undissociated O_2 -molecule, on being raised to a certain moderately high temperature in the flame, has its "residual affinities" sufficiently stimulated to enable it to seize upon, and grip hold of, two undissociated hydrogen molecules, forming initially an unstable vibratory complex H_4O_2 , thus:—



(b) which, seizing upon two H_2 molecules, would momentarily form the unstable complex,

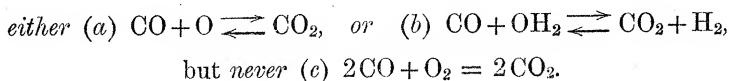


(8) Such a complex, being in an intensely vibratory condition, would instantly break down, partly (i) into two molecules of steam, also in a vibratory condition, and therefore chemically "activated," and partly also (ii) into two H_2 -molecules and two O atoms, thus:—



The ratio $(n/100-n)$ would obviously depend upon both temperature and environment; the higher the temperature, and the less hydrogen in the environment, the less the magnitude of n . In some such way, however, it may be supposed that hydrogen, in a combustible mixture containing also CO, could function as a resolver of O_2 molecules simultaneously into (i) "activated" steam and (ii) O atoms.

(9) It is also further supposed that O_2 and CO molecules are mutually inert in flames, and that, before the latter can be oxidised, the O_2 must be resolved either into atoms or "activated" steam; thus, we might have:—



(10) Such a view would account for (a) the comparative slowness of the combustion of carbon monoxide, as illustrated by the slow rise in the pressure curve for the CO-air mixtures in our experiments; (b) the observed accelerating influence of both steam and hydrogen thereon; and (c) the fact that the "mass influence" of carbon monoxide upon the actual distribution of oxygen between the combustible constituents of a burning mixture is

proportional to the *first* power (and not, like that of hydrogen, to the *square*) of its concentration.

(11) The remarkable influence of hydrogen upon the rate of combustion of carbon monoxide in our experiments calls to mind the similar influence of steam first discovered by H. B. Dixon in the year 1880. In his later experiments upon the rates of detonation of $(2\text{CO}_2 + \text{O}_2)$ mixtures containing varying proportions of steam, Dixon found that, starting with a well-dried mixture (fired at a pressure of 760 mm.), the rate increased, with successive additions of moisture, from 1264 to a maximum of 1738 metres per second for a mixture saturated with moisture at 35°C ., and therefore containing about 5.5 per cent. of steam.* He also found that, on sparking a well-dried mixture of carbon monoxide (60 per cent.), chlorine peroxide (29 per cent.), and oxygen (11 per cent.), though a flame was propagated through the gases, as much as 76 per cent. of the original carbon monoxide may remain unburnt,† showing that, whilst dry “nascent” oxygen may be reactive towards carbon monoxide, some other condition (*e.g.*, its continuous reproduction at a high enough temperature) is needed to make it fully effective. Our experiments seem to point to hydrogen being even more potent than its equivalent of steam as a promoter of the combustion of carbon monoxide (though this is a matter needing further investigation), and they suggest that its primary function is to resolve continuously the inert O_2 molecule into an “active” oxidising condition (*i.e.*, into O atoms and “activated” OH_2), itself being continuously regenerated in some such manner as we have described.

(12) In addition to their bearing upon the theory of gaseous combustion, our results are of practical interest in connection with a question which has recently been much under discussion. In certain quarters it has become fashionable to assume that the relative values of different combustible gases are strictly proportional to their heats of combustion, irrespective of their chemical characters or modes of combustion. Such an assumption was, indeed, “tentatively accepted” by the Fuel Research Board in their “Report on Gas Standards” in 1919, although its endorsement was qualified by the admission that “experimental proof” of it “is still incomplete.”‡ It seems difficult to reconcile it with the cumulative results of the last forty years of scientific research upon gaseous combustion, which have shown more and more clearly that the fundamental properties of the explosive mixtures formed by different combustible gases with air, arising from their own peculiar chemical characters

* H. B. Dixon, ‘Phil. Trans.’ A, vol. 184, p. 187 (1893).

† H. B. Dixon and E. J. Russell, ‘Trans. Chem. Soc.’ vol. 71, p. 605 (1897).

‡ Cmd. 108, p. 5.

and compositions, do affect profoundly their economic uses. The results of the present research emphasise the importance of the chemical composition of a combustible gas (or mixture) as a factor which cannot be disregarded when its economic value is in question.

Further experiments at high pressures are in contemplation to develop the matters dealt with in this paper; and it is intended also to make similar experiments at atmospheric pressure.

Our thanks are due (*a*) to the Government Grant Committee of the Society for grants out of which the cost of the expensive apparatus employed in the research has been defrayed, and (*b*) to the Salters' Institute of Industrial Chemistry for the Fellowship granted to one of us (W. A. H.) to enable him to devote his whole time to the work.

On the Spectra of Lead Isotopes.

By T. R. MERTON, F.R.S.

(Received July 12, 1921.)

In a previous communication* an account was given of comparative measurements of the wave-length of the line $\lambda = 4058 \text{ \AA}$, in the spectra of ordinary lead and of the leads obtained from uranium and thorium minerals respectively. The line $\lambda = 4058 \text{ \AA}$ is the strongest line in the arc spectrum of lead and the results obtained were

$$\lambda (\text{lead from pitchblende}) - \lambda (\text{ordinary lead}) = 0.0050 \pm 0.0007 \text{ \AA}.$$

$$\lambda (\text{ordinary lead}) - \lambda (\text{lead from thorite}) = 0.0022 \pm 0.0008 \text{ \AA}.$$

The lead from pitchblende had been extracted from some Joachimstal pitchblende residues, and since this mineral is known to be free from thorium there was no reason to suspect that the sample of lead obtained was contaminated with lead of a thorium parentage. It was not known whether any ordinary lead was present but the wave-length difference which was found agreed closely with the value found by Aronberg* in a comparison of the same spectrum line of ordinary lead and a sample of lead from Australian Carnotite for which Prof. Richards had found an atomic weight of 206.318.

* 'Roy. Soc. Proc.,' A, vol. 96, p. 388 (1920).

† 'Astrophys. Journ.,' vol. 27, p. 96 (1918).